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RUBIDIUM-RICH FELDSPARS IN A GRANITIC PEGMATITE FROM THE KOLA PENINSULA, RUSSIA

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Abstract

Analysis of minerals associated with end-member pollucite in a rare-element granitic pegmatite from the Kola Peninsula, in Russia, has revealed two populations of Rb-rich feldspar. A 1 mm-wide vein of non-perthitic microcline cross-cutting the pollucite has an average of 8.21 wt.% Rb_2O and a unit formula of $(Na_{0.022}K_{0.696}Rb_{0.256}Cs_{0.014})(Al_{1.004}Si_{2.981}P_{0.015})O_8$, corresponding to 26 mol.% content of Rb-feldspar. Small (≤15 μm) grains of a Rb-dominant feldspar dispersed throughout the pollucite have an average of 24.39 wt.% Rb_2O, 0.02 Na_2O, 2.02 K_2O, 0.59 Cs_2O, 0.10 P_2O_5, 15.86 Al_2O_3, 56.75 SiO_2, sum 99.79. The unit formula $(K_{0.136}Rb_{0.831}Cs_{0.013})(Al_{0.990}Si_{3.006}P_{0.004})O_8$ indicates 82 mol.% of Rb-feldspar. Analysis of individual grains gives a maximum of 26 wt.% Rb_2O, corresponding to 91 mol.% Rb-feldspar. This is the highest Rb content of any known mineral. The Cs_2O content attains 1.00 wt.%, corresponding to 2.1 mol.% Cs-feldspar. Activity of Rb^+ must have been exceptionally high during late stages of crystallization of the parent pegmatite: pollucite has the highest recorded Rb content (2.8 wt.% Rb_2O; 10 mol.% $RbAlSi_2O_6$) and lepidolite has up to 6.5 wt.% Rb_2O.

Keywords: alkali feldspar, microcline, rubidium, pollucite, lepidolite, granitic pegmatite, Kola Peninsula, Russia.

Sommaire

Une analyse chimique des minéraux qui sont associés à la pollucite pure provenant d'une pegmatite granitique enrichie en éléments rares de la péninsule de Kola, en Russie, révèle deux populations de feldspath riche en Rb. Une veinule millimétrique de microcline non perthitique qui recoupe la pollucite contient, en moyenne, 8.21% de Rb_2O, ce qui donne une formule structurale $(Na_{0.022}K_{0.696}Rb_{0.256}Cs_{0.014})(Al_{1.004}Si_{2.981}P_{0.015})O_8$, et donc 26% de feldspar rubidique. De petits grains (≤15 μm) d'un feldspath à dominance de Rb sont dispersés dans la pollucite; ils contiennent, en moyenne, 24.39% de Rb_2O, 0.02% de Na_2O, 2.02% de K_2O, 0.59% de Cs_2O, 0.10% de P_2O_5, 15.86% de Al_2O_3, et 56.75% de SiO_2, pour un total de 99.79%. Dans ce cas, la formule structurale, $(K_{0.136}Rb_{0.831}Cs_{0.013})(Al_{0.990}Si_{3.006}P_{0.004})O_8$, indique 82% (base molaire) de feldspath rubidique. La teneur dans certains grains atteint 26% Rb_2O, correspondant à 91% du pôle Rb. Il s'agit de la teneur en Rb la plus élevée qui soit connue dans un minéral. La teneur en Cs atteint 1.00% de Cs_2O, ce qui correspond à 2.1% du pôle césique. La concentration du Rb a dû être anormalement élevée au cours des stades finaux de la cristallisation de la pegmatite hôte, comme en témoigne la teneur très élevée en Rb de la pollucite (2.8% Rb_2O en poids, 10% $RbAlSi_2O_6$, base molaire) et de la lépidolite (jusqu'à 6.5% Rb_2O).

(Traduit par la Rédaction)

Mots-clés: feldspath alcalin, microcline, rubidium, pollucite, lépidolite, pegmatite granitique, péninsule de Kola, Russie.

Introduction

Rubidium-rich alkali feldspar occurs in highly fractionated rare-element granitic pegmatites, particularly in those of the complex type that contain pollucite. Previous to this work, the highest Rb content of a natural feldspar known was measured by atomic absorption spectroscopy of a bulk sample of microcline from Red Cross Lake, Manitoba (5.9 wt.% Rb_2O: Černý *et al.* 1985). Subsequent microbeam analysis indicated even higher concentrations of Rb in late hydrothermal generations of alkali feldspar closely associated with pollucite (Teertstra *et al.* 1993). This prompted us to initiate a systematic study of Rb-bearing K-feldspar from near the core zones of complex rare-element granitic pegmatites; see Černý (1991) for the classification of granitic pegmatites. Back-scattered electron imaging and quantitative electron-microprobe analysis have revealed multiple generations of (K,Rb)-feldspar at many localities.

For the first time, we report here in detail on a Rb-dominant feldspar which also is the most Rb-rich mineral so far encountered. Two generations of (K,Rb)-feldspar, which average 26 and 82 mol.% Rb-feldspar, formed during the alteration of pollucite from a rare-element pegmatite in the Kola Peninsula.

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The second-generation feldspar attains locally as much as 91 mol.% Rb-feldspar, and is the most Rb-dominant feldspar we have so far examined.

Locality and Sample Description

The sample was obtained from the collections of the Ecole des Mines, Paris for the study of pollucite (Teertstra & Černý 1995). The locality of our sample is described as the Kola Peninsula, but the specific locality is unknown. At least two pollucite-bearing pegmatites have been described from the Kola Peninsula (Kuzmenko 1976), but so far they have not been fully identified in the literature (*e.g.*, Gordiyenko 1973, Voloshin *et al.* 1981). Circumstantial evidence suggests that our pollucite samples may have come from the same locality as the pollucite analyzed by Panasenko & Goroshchenko (1970; *cf.* Teertstra & Černý 1995).

The sample consists of translucent to cloudy white pollucite veined by purple mica. Examination of polished thin sections shows two generations of Rb-enriched feldspar. The first generation is a (K,Rb)-feldspar that participates in sequential veining of pollucite by quartz (± lepidolite), microcline (+ lepidolite) and lepidolite (± quartz). A 1-mm-wide microcline vein has faintly visible cross-hatched twinning in cross-polarized light, is nonperthitic, and is associated with lepidolite and recrystallized pollucite (Fig. 1). Structure refinement of a single crystal of this feldspar confirmed its triclinic symmetry. Late thin veins of fine-grained muscovite and spodumene locally cross-cut the pollucite. The second generation is a (Rb,K)-feldspar located along contacts of these veins with pollucite, and as small (<0.5 mm) clusters fully embedded in the pollucite and associated with albite. Low abundance and a grain size of less than 15 μm preclude characterization of the Rb-richest feldspar by optical microscopy or X-ray diffraction. However, late generations of nonperthitic Na-poor (K,Rb)-feldspar are a common product of low-temperature metasomatic alteration of pollucite (Teertstra *et al.* 1993, Teertstra & Černý 1995). The perfect stoichiometry of this feldspar mineral, and its paragenetic and textural analogy with many other Rb-rich to Rb-dominant feldspars from other localities, which have been verified either optically or by X-ray diffraction, leave no reasonable doubt as to its nature.

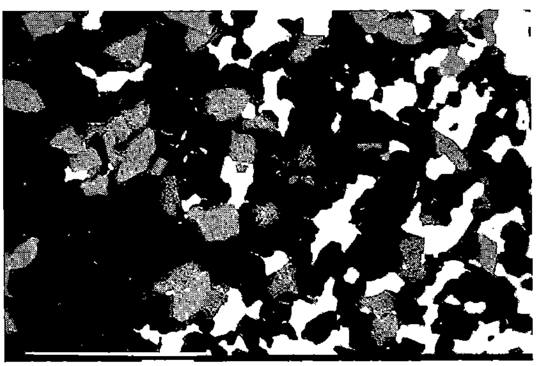


Fig. 1. Back-scattered electron images of minerals in the sample of granitic pegmatite from Kola. Margins of the vein of rubidian microcline (dark grey) have numerous inclusions of pollucite (white) and lepidolite (grainy grey + white). The scale bar is 100 μm in length.

Analytical Method

The chemical composition of the feldspar was determined using wavelength-dispersion spectrometry (WDS) on a CAMECA SX–50 electron microprobe (EMP) operating at 15 kV and 20 nA, with a beam diameter of 5 μm. Data were reduced using the PAP procedure of Pouchou & Pichoir (1985). The concentration of minor elements was measured using albite (Na$K\alpha$), pollucite (Cs$L\alpha$), $SrTiO_3$ (Sr$L\alpha$), and VP_2O_5 (P$K\alpha$). The elements Fe, Mg, Ba, Ti, F, Mn, Ga, Ca, and Pb were sought, but not detected.

Initial analysis of the major elements (K, Rb, Al, Si) using the rubidian microcline from Red Cross Lake as a standard gave poor results. A small cluster of Rb-rich feldspar grains in the Kola pollucite was then used as a standard for Rb, Al, Si, and orthoclase for K. The results were much better but still not satisfactory. The final approach used synthetic $Rb_2ZnSi_5O_{12}$ glass (Rb$L\alpha$) (Kohn *et al.* 1994) and gem sanidine (K$K\alpha$, Al$K\alpha$, Si$K\alpha$) from the Volkesfeld area, Eifel, Germany (Bernotat-Wulf *et al.* 1988) as standards. The composition of the standard sanidine was derived by assuming that measurements of the concentrations of the minor elements Sr, Ba, Na and Fe were accurate; K, Al and Si values were calculated for agreement with stoichiometric requirements of the general formula for a feldspar. The accuracy of the standard was then tested by cross-analysis with other well-characterized minerals [*cf.* Teertstra *et al.* (1998) for details].

Results

The final analytical approach gave excellent agreement with the stoichiometric requirements of the general feldspar formula, as shown by the representative compositions in Table 1. Individual values of the framework charge TO_2^- of 0.987(8) (expressed as Al – P to compensate for the berlinite substitution $AlPSi_{-2}$) and M-cation charge (M^+) of 0.987 (8) are equal within error (Fig. 2A). Data are clustered about a mean (Si + 2P) value of 3.013(7) atoms per formula unit (*apfu*), but the sum of the T cations is 4.000(2) *apfu* (Fig. 2B). Values are constrained to lie

TABLE 1. CHEMICAL COMPOSITION AND UNIT FORMULAE OF (K,Rb)-FELDSPAR FROM A GRANITIC PEGMATITE, KOLA PENINSULA, RUSSIA

	1	2	3	4	5	6
SiO_2 wt.%	61.15	60.68	61.56(0.59)	57.37	55.73	56.75(0.68)
Al_2O_3	17.87	17.74	17.59(0.17)	16.14	15.67	15.86(0.17)
P_2O_5	0.32	0.31	0.37(0.16)	0.02	0.06	0.10(0.09)
Na_2O	0.31	0.31	0.23(0.09)	0.64	0.00	0.02
K_2O	11.40	11.07	11.26(0.40)	2.69	0.99	2.02(0.55)
Rb_2O	7.95	8.51	8.21(0.49)	22.44	26.12	24.39(1.03)
Cs_2O	0.73	1.00	0.68(0.17)	0.52	0.65	0.59(0.15)
SrO	0.07	0.05	0.02(0.01)	0.07	0.02	0.05
sum	99.84	99.86	99.90(0.74)	100.11	99.24	99.79(0.97)
atomic contents (*apfu*) normalized to 8 atoms of oxygen						
Si	2.962	2.961	2.981(0.013)	2.994	3.003	3.006(0.011)
Al	1.026	1.026	1.004(0.007)	0.999	0.995	0.990(0.010)
P	0.013	0.013	0.015(0.006)	0.001	0.003	0.004(0.004)
Na	0.029	0.029	0.022(0.009)	0.065	0.000	0.001
K	0.709	0.693	0.696(0.022)	0.180	0.068	0.136(0.037)
Rb	0.249	0.269	0.256(0.017)	0.758	0.905	0.831(0.036)
Cs	0.015	0.021	0.014(0.003)	0.012	0.015	0.013(0.003)
Sr	0.002	0.001	0.001	0.002	0.001	0.000
ΣM	1.004	1.013	0.987(0.007)	1.018	0.988	0.983(0.010)
M^+	1.006	1.015	0.988(0.007)	1.021	0.989	0.986(0.010)
TO_2^-	1.013	1.014	0.988(0.005)	1.000	0.992	0.986(0.009)
ΣT	4.002	4.000	4.000(0.002)	3.995	4.001	4.000(0.003)

1, 2. Microcline vein in pollucite.
3. Average composition of microcline (N = 8); 1σ standard deviations are shown in parentheses.
4, 5. Rb-dominant feldspar from clusters in pollucite.
6. Average composition of Rb-dominant feldspar (N = 9); 1σ standard deviations are shown in parentheses.

near the origin of the plagioclase-like substitution and have minor (~1%) $\square Si_4O_8$ substitution (vectors 1 and 2, respectively, in Fig. 2B).

There are two distinct populations of feldspar compositions: one that characterizes the microcline veinlet and averages 26 mol.% Rb-feldspar (generation 1), and one that averages 82 mol.% Rb-feldspar and corresponds to the dispersed clusters of Rb-dominant feldspar (generation 2). Compositions in this second population extend to Rb = 0.91 *apfu*, with K as low as 0.07 *apfu* (Fig. 3A). Both populations have mean values of $(M^+) - (Al - P)$ near 0 *apfu*, *T*-cation sums (Al + Si + P ± Fe) near 4.000 *apfu*, and *M*-cation sums slightly less than 1.00 *apfu* (Table 1). The veinlet microcline has minor substitution of $(AlP)Si_{-2}$, with up to 0.55 wt.% P_2O_5, but P substitution is negligible in the Rb-dominant feldspar. Cs seems to show a slight positive correlation with Rb in each population, but the overall concentration of Cs is about the same in both populations (Fig. 3B). The feldspar richest in Rb has up to 1.00 wt.% Cs_2O (anal. 2, Table 1), corresponding to 0.021 Cs *apfu* (2.1 mol.% Cs-feldspar). This is the highest Cs content ever reported for a feldspar. Overall, feldspar compositions closely follow the ideal stoichiometry of the $KAlSi_3O_8 - RbAlSi_3O_8$ series.

Discussion

Gordiyenko & Kamentsev (1967) reported 4.1 wt.% Rb_2O and 0.5 wt.% Cs_2O in a (presumably) primary blocky K-feldspar from a pegmatite in the Kola Peninsula, but compositions of feldspar veins in pollucite have not been reported by any of the Kola

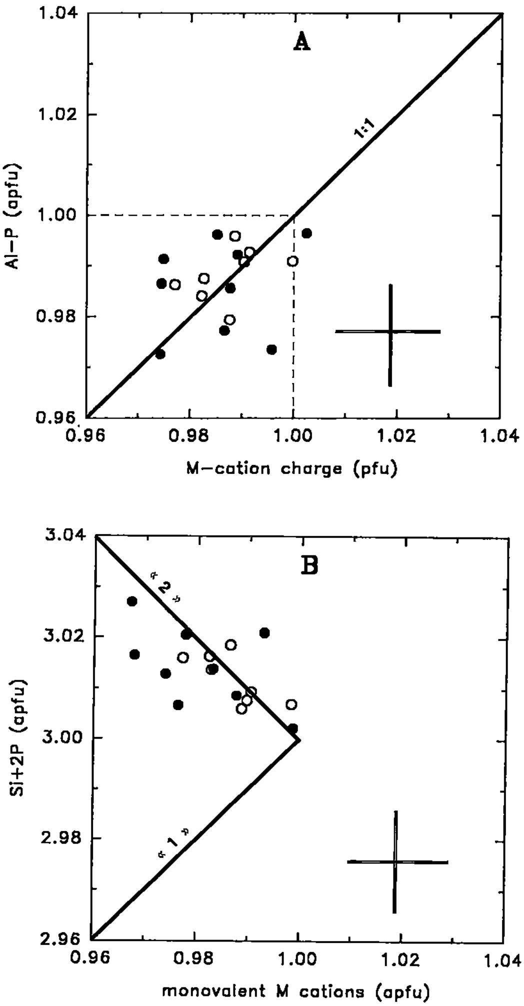
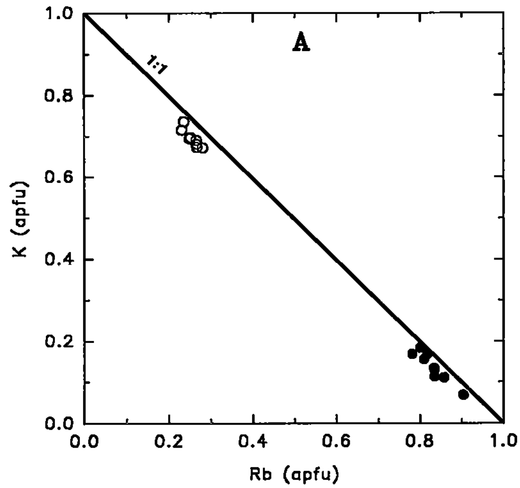


FIG. 2. Element variation in the feldspar-group minerals in the sample. (A) (Al–P) *versus* *M*-cation charge, with a 1:1 ratio indicated; (B) (Si + 2P) *versus* monovalent *M*-cations with vectors drawn for (1) the plagioclase substitution and (2) the $\square Si_4O_8$ trend. Crossbars indicate counting precision for the Eifel sanidine standard. Symbols: Generation 1 (°) and generation 2 (•) feldspars.



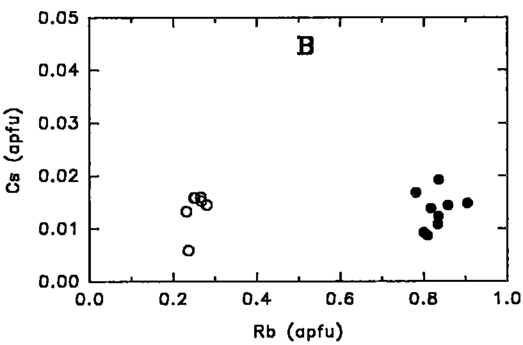


FIG. 3. Variation in alkali concentrations in feldspar-group minerals in the sample. (A) K *versus* Rb, with the line indicating $\Sigma M = 1$. (B) Cs *versus* Rb. Symbols as in Figure 2.

investigators. The Rb (and Cs) contents of both the nonperthitic microcline and the Rb-dominant feldspar examined here exceed those of any feldspar previously reported, including the intermediate microcline from Red Cross Lake, Manitoba (Černý *et al.* 1985).

As mentioned above, considerable enrichment in Rb commonly occurs in veinlets and clusters of late-stage K-feldspar in pollucite from many localities. However, the extreme enrichment of the feldspar reported here surpasses the Rb contents of most other feldspars examined to date. This level of enrichment presumably reflects an exceptionally high level of Rb in the parent pegmatite, particularly during the near-solvus and subsolidus stages. This reconstruction is strongly suggested also by the compositions of even the few associated minerals in our sample. The host pollucite has the highest Rb content known to date for this mineral (up to 2.8 wt.% Rb_2O, Teertstra & Černý 1995), and the associated micas are also rich in Rb. Muscovite contains 3.82–3.99 wt.% Rb_2O, 0.39–1.08 Cs_2O and 0.42–0.67 wt.% F, corresponding to 17–18 at.% Rb and 0.6–1.1 at.% Cs at the interlayer site and 4.5–7.2 at.% F at the (F,OH) site, respectively. The zoned lepidolite has 5.51–6.53 wt.% Rb_2O, 1.08–3.23 Cs_2O and 1.89–8.54 wt.% F, corresponding to 27–29 at.% Rb and 3.2–9.4 at.% Cs at the interlayer site and 22–99 at.% F at the (F,OH) site, respectively.

The two feldspars described here are likely not in equilibrium, as indicated by their separation in space and time and by their distinct P contents. Neither of them coexists with another feldspar phase with a distinctly different K/Rb ratio, as encountered at other localitites (Teertstra *et al.* 1993, Teertstra & Černý 1995). If in equilibrium, such assemblages might suggest the existence of a solvus at appreciably low temperature, below the limit of practical experimental work (~400°C; M. Lagache, pers. commun. 1994). Otherwise, the compositional heterogeneity at other localities, and the remarkable difference between the two feldspars in the sample, would indicate considerable fluctuations in the concentration of Rb^+ in a late fluid. In any case, the Rb partition coefficient of 0.28 between a hydrothermal solution at 180°C and K-feldspar (Pauwels *et al.* 1989) and the high Rb content of our feldspar suggest an extremely high activity of Rb at low-temperature subsolvus conditions in the parent pegmatite.

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